BAND ANTI-CROSSING MODELLING AND CHARACTERIZATION OF MULTI QUANTUM WELL GAINNAS FOR PHOTOVOLTAIC APPLICATION

MUHAMMAD IZZUDDIN BIN ABD SAMAD

A thesis submitted in
fulfilment of the requirement for the award of the
Degree of Master of Electrical Engineering

Faculty of Electrical and Electronic Engineering
Universiti Tun Hussein Onn Malaysia

JANUARY 2021

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged.

Student : ……………………………………………………

MUHAMMAD IZZUDDIN BIN ABD SAMAD

Date : ……………12 JANUARY 2021……………

Supervisor : ……………………………………………………

DR. KHAIRUL ANUAR BIN MOHAMAD

This thesis work is dedicated to my family, my supervisor and my friends.

ACKNOWLEDGEMENT

In the name of ALLAH, the Most Beneficent and the Most Merciful, Alhamdulillah, all praises to ALLAH for the strengths and His blessing in completing this research. I am very thankful to my supervisor, Dr. Khairul Anuar Bin Mohamad, for his guidance, advice and encouragement throughout my master's studies. I would like to thank Dr. Mohammad Syahmi Bin Nordin from University of Essex and Dr. Afishah Binti Alias from Faculty of Applied Science and Technology (FAST), UTHM, who helped me a lot in the theoretical and experiment works.

My special thanks go to all current postgraduate students of Microelectronic and Nanotechnology–Shamsuddin Research Centre at Universiti Tun Hussein Onn Malaysia, Dr. Megat Muhammad Ikhsan Megat Hasnan Mrs. Anis Suhaili Bakri, Mrs. Nur Amaliyana Raship, Ms. Nur Liyana Razali, Ms. Nur Zehan An'nisa Md Shah, Ms. Fatin Nor Ahmad, Mr. Yusmar Palapa and Mr. Zulkifli Azman, for their help on the technical support.

Finally, I am forever indebted to my wonderful parents (Abd Samad and Siti Rohaya) for their everlasting love, support and prayers that make this dream come true. Thanks to all my siblings (Nur Afifah, Nur Fariha, Nur Syafiqah, Muhammad Adib Firdaus and Muhammad Adam), without their encouragement, support and understanding, it would have been impossible for me to complete my studies.

ABSTRACT

A recent study of $Ga_{0.952}In_{0.048}N_{0.016}As_{0.984}$ /GaAs multi-quantum-well (MQW) p-i-n diode has reported that it is able to operate in near-infrared applications (800-1100nm). Nevertheless, there is no elucidations on the effect of indium (In) and nitrogen (N) fractions on electronic band transition, the localisation defect, and the impact of mesa active area on the electrical and photo-electrical properties of a diode. Hence, our motivations are simulating the GaInNAs electronic band transition, analyse the localisation defect and investigate an impact of mesa active area on the diode properties. The band anti crossing (BAC) modelling has been used to illustrate the GaInNAs electronic band transition with a bowing mechanism and resulted the relationship of redshift GaInNAs versus temperature. At the same time, temperature dependence photoluminescence (PL) measurement was used to validate the BAC modelling result and identify localisation defect at low temperature. Then, the connectivity between BAC and PL results was determined through Varshni analysis. The Varshni results were found synergies each other by close values of the temperature coefficient and GaInNAs energy bandgap at 0 K. On the other hand, an anomalies PL peaks energy at low temperature has been identified and indicated presence localisation defect. Next, the localisation energy parameter had been quantified via localisation energy analysis. The localisation energy parameters are resulted with maximum localisation energy = 9.44 eV at maximum localisation temperature = 40 K and delocalisation temperature =100 K. Furthermore, an investigation on the effect of the mesa active area on diodes were conducted using current-voltage measurements under dark and illumination. An increasing mesa active area was found increment in the dark current and ideality factor, while the value of short-circuit current density and efficiency parameters (photovoltaic) were decreased likewise. However, the value of turn on voltage, barrier height, open-circuit voltage and fill factor have constantly recorded and unaffected by increment of mesa active area.

ABSTRAK

Dalam kajian baharu ini, $Ga_{0.952}In_{0.048}N_{0.016}As_{0.984}$ /GaAs p-i-n diod berbilang lapisan telaga quantum mencatatkan kebolehupayaan dalam aplikasi optoelektronik gelombang inframerah dekat (800-1100nm). Walaupun begitu, masih tiada penjelasan terhadap kesan perubahan nilai jurang tangga tenaga, kesan setempat dan impak keluasan aktif mesa terhadap ciri-ciri diod. Oleh itu, matlamat kajian ini adalah untuk menjalankan simulasi perubahan jurang tenaga, menganalisa kesan setempat dan mengkaji kesan luas aktif mesa terhadap ciri-ciri diod. Hasil pemodelan jalur anti silang (BAC) dapat menggambarkan perubahan transaksi jurang tenaga dengan mekanisme melengkung dan menentukan kolerasi perubahan merah jurang tenaga GaInNAs terhadap suhu. Selain itu, hasil kajian pengukuran suhu kefotopendarcahayaan (PL) dengan pengantungan suhu digunakan untuk mengesahkan hasil pemodelan BAC dan mengenalpasti kesan setempat pada suhu yang rendah. Seterusnya, analisa Varshni dijalankan untuk menentukan perhubungan di antara hasil kajian BAC dan PL. Didapati, dua hasil tersebut mempunyai kesenergian dengan nilai bacaan pekali suhu dan jurang tenaga GaInNAs pada 0 K. Di samping itu, kesan anomali puncak tenaga PL pada suhu yang rendah dikenalpasti dan menunjukan kehadiran kecacatan kesan setempat. Seterusnya, parameter kuasa setempat dikuantifikasi melalui analisa kuasan setempatan. Oleh itu, parameter tenaga setempat bagi bahan ini dikuantifikasikan dengan tenaga setempat maksimum = 9.44 eV , suhu setempatan maksimum = 40 K dan dan suhu nyahsetempat = 100 K. Selain itu, ujikaji terhadap pengaruh luas aktif mesa terhadap ciri-ciri diod dinilai dengan menggunakan pengukuran arus-voltan dalam keadaan gelap dan pencahayaan. Peningkatan keluasan aktif mesa dapat meningkatkan arus gelap dan faktor idealisasi, tetapi nilai parameter ketumpatan litar arus yang tinggi dan parameter kecekapan didapati mengurang. Selain itu, nilai parameter voltan arus buka, ketingian sawar, voltan litar buka dan faktor penuh mencatatkan dengan nilai yang sama dan tidak terkesan dengan peningkatan keluasan aktif mesa.

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LIST OF SYMBOLS AND ABBREVIATIONS

α	-	Temperature coefficient
α_{GaAs}	-	Temperature coefficient of GaAs
α_{InAs}	-	Temperature coefficient of InAs
β	-	Debye temperature
β_{GaAs}	-	Debye temperature of GaAs
β_{InAs}	-	Debye temperature of InAs
β_{InN}	-	Debye temperature of InN
β_{GaN}	-	Debye temperature of GaN
ε_{fm}	-	Fermi level of metal
η	-	Efficiency
Φ_b	-	Barrier height
$\emptyset_m$	-	Work function of a metal
$\emptyset_s$	-	Work function of a semiconductor
A	-	Active area
$A*$	-	Richardson constant
As	-	Arsenic
B	-	Binary parameters
BAC	-	Band Anti-Crossing
Be	-	Beryllium
C	-	Bowing parameter
$\mathrm{C_{nm}}$	-	Coupling parameter
DBR	-	Distributed Bragg's reflector
E_g	-	Energy band gap
E_N	-	Localisation state of nitrogen
$\mathrm{E_M}$	-	Extended conduction band of GaInAs
$\mathrm{E_-}$	-	Red-shift band gap

E_+	-	Blue-shift band gap
$E_\pm$	-	Eigenvalue expression
E^0	-	Energy band gap at 0 K
E^0_{GaAs}	-	Energy band gap of GaAs at 0 K
E_{InAs}	-	Energy band gap of InAs at 0 K
$E_{Ga_{1-x}In_xAs}$	-	E_M without wavevector
E_{maxloc}	-	Maximum localisation energy
$E^0_{GaInNAs}$	-	Energy band gap of GaInNAs at 0 K
$E_{GaInNAs}$ (RT)	-	Energy band gap of GaInNAs at room temperature
E_{maxloc}	-	Maximum localisation energy
E_{Loc}	-	Localisation energy of GaInNAs
$E_{Varshni}$	-	Energy of GaInNAs from Varshni fitting
E_{PL}	-	Energy of GaInNAs from PL peak measurement
FF	-	Fill factor
FWHM	-	Full-width-at-half-maximum
Ga	-	Gallium
GaInNAs	-	Dilute nitride
I_0	-	Leakage current
I_s	-	Saturation current
I_{sc}	-	Short-circuit current
In	-	Indium
InP	-	Indium Phosphorus
J	-	Dark current density
J_{O1}	-	Saturation current density
J_{O2}	-	Leakage current density
J_{sc}	-	Short-circuit current density
J_{mp}	-	Maximum short-circuit current density
K	-	Kelvin
k	-	Wavevector
k	-	Boltzmann's constant
LPE	-	Liquid-phase epitaxy
LED	-	Light-emitting diode
MQW	-	Multi-Quantum Well

MBE	-	Molecular beam epitaxy
MOCVD	-	Metal-oxide chemical vapour deposition
MS	-	Metal-semiconductor
N	-	Nitrogen
n	-	Ideality factor
PL	-	Photoluminescence
q	-	Charge
Q	-	Quaternary linear interpolation scheme
QW	-	Quantum well
R_s	-	Series resistance
RCEPD	-	Resonant-cavity-enhanced photodiode
SBD	-	Schottky barrier diode
SCR	-	Space charge region
t	-	Ternary linear interpolation scheme
T	-	Temperature
TE	-	Thermionic emission
T_{maxloc}	-	Maximum localisation temperature
T_{deloc}	-	Delocalisation temperature
T_{Loc}	-	Localisation temperature
VRCEPD	-	Vertical resonant-cavity-enhanced photodiode
w	-	Barrier width of semiconductor
V	-	Voltage bias
V_t	-	Turn-on voltage
V_{mp}	-	Maximum voltage
V_{oc}	-	Open-circuit voltage
V_D	-	Potential barrier
V_{bi}	-	Built-in potential
X	-	First mole fraction
x	-	Indium fraction
x_s	-	Electron affinity
γ	-	Fitting parameter
y	-	Nitrogen fraction
Y	-	Second mole fraction

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`CHAPTER 1

INTRODUCTION

1.1 Research background

Optoelectronic devices are electrical-to-optical or optical-to-electrical transducers, such as solar cells, photodiodes, light-emitting diodes (LEDs) and laser diodes [1]. Throughout the decade, high-performance optoelectronic devices have been aggressively pursued to support the future generation of applications [2]. Basically, an Indium-phosphate (InP) material based was commonly used in infrared devices either at near infrared range (medical photodiode) or middle infrared range (telecommunication). Although InP based material can be operated on the infrared range, this material has disadvantages fabrication cost and the non-monolithic growth process. Hence, dilute nitride material was introduced as alternative material to InP-based optoelectronic devices [3].Fundamentally, dilute nitrides material could be epitaxially grown by Gallium (Ga), Indium (In), Arsenic (As) and Nitrogen(N) such as GaN, GaNAs and GaInNAs [3]. So, this research is focused on the GaInNAs 10 multi-quantum-wells (MQWs) p-i-n design to operate on near infrared range.

In other words, the In and N compositions in GaInNAs material have significantly impacted on the devices operating wavelength. If the high In (higher than 30%) and high N (higher than10%) fraction use for middle infrared range, while the low In (lower than30%) and N (lower than 10%) fraction use for near infrared range [4]. Fundamentally, the GaInNAs bandgap could be determined through Vegard law numerical modelling [4] . The energy bandgap and temperature relationship was able to verified by using Varshni equation [3]. But these numerical modelling have a limitation in illustrating the electronic band transition. Meanwhile, the Band Anti Crossing (BAC) modelling was employed to modelling the transition bandgap [4].

An implementation of a MQWs in an intrinsic region of the p-i-n diode is used to enhance the photocurrent production, emission/absorption mechanism and quantum efficiency [3]. In diode design, MQWs design usually used to reduce dark current [5], while it could be enhanced thermal quenching of excitons [6] and photogenerated electron [7]. So, an implementation of MQWs in a dilute nitride devices was focused on the spectral response and detectivity characteristics, especially as a photodetector [8].

The MQWs dimension was able be affected the operational wavelength in a bias condition and the localisation mechanism at low temperature [5]. Furthermore, the localisation defect also could be traced via photoluminescence (PL) peaks energy by examine temperature dependence PL measurement [9]. In addition, the photocurrent oscillation characterisation on $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$ 10-MQW p-i-n diode had identified the thermal carriers escape time on a MQW structure at low temperature, which is related to localisation defect [9].

On the other hand, the comparison study on $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$ with 10-MQW and 20-MQW-based p-i-n diode was conducted to study impact of number QWs to dark current and photocurrent [10]. These studies were found that the leakage current of the 10-MQW is lower than the 20-MQW, while the 20-MQW photocurrent was higher than 10-MQW. These results had been influencing by the internal resistance on the intrinsic layer of the diode. Meanwhile, the dark current and photogenerated current also can be affected on the active area of a diode by an electric field propagation during carrier transportation.

Hence, our research interested to model the electronic band transition of GaInNAs material via BAC modelling. This modelling is used to estimate the energy bandgap of GaInNAs and verify the correlation between GaInNAs bandgap with temperature. On the other hand, the temperature dependence PL measurement and localisation energy analysis were used to determine the optical characteristics of $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$ 10-MQW p-i-n thin film and localisation energy parameters, respectively. Nevertheless, an active area study on the electrical, metal semiconductor (MS) contact and photo-electrical characteristics of diode were conducted to investigate the impact mesa active area on the carrier transportation under dark and illumination. While. The MS contact analysis was employed in determining whether a diode is an ideal diode via the thermionic emission (TE) theory numerical analysis.

1.2 Problem statement

A decade ago, most studies were interested in the development of GaInNAs/GaAs for the terahertz signal communication with higher In and N composition [3], [8]. In recent research, a low In and N composition of a GaInNAs/GaAs device is able to work in a near-infrared optoelectronic device for space solar cell [11]–[13] and photodiode [14], [15]. The estimation the energy bandgap of the GaInNAs material and the optimising In and N fractions for achieving lattice mismatch GaInNAs/GaAs thin film were calculated by using Vegard law. However, the Vegard law and Varshni equation have a limitation to illustrate the GaInNAs electronic band transition and only be modelled the GaInNAs energy bandgap. So, this research was interested to model the electronic band transition of GaInNAs material via BAC modelling. This modelling is used to estimate the energy bandgap of GaInNAs and verify the correlation between GaInNAs bandgap with temperature.

In previous study, an optical characteristics $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$/GaAs 10-MQW p-i-n thin film has been characterised using PL measurement at 300 K, it energy bandgap was 1.152 eV of energy band gap which equivalent to 1076 nm [10]. Moreover, the temperature dependent photocurrent oscillation characterisation on $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$ 10-MQW p-i-n diode had identified the thermal carriers escape time at low temperature and related to localisation defect [9]. Hence, this study motivated to conduct the temperature dependence PL measurement and localisation energy to determine the optical characteristics of $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$ 10-MQW p-i-n thin film and localisation energy parameters, respectively.

Furthermore, the comparison study on $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$ with 10-MQW and 20-MQW-based p-i-n diode had found the effect of number QWs to dark current and photocurrent [10]. An increasing number of QWs had been reduced dark current and enhance the photocurrent. But impact of active area on the $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$ 10-MQW diode properties still unrevealed, this investigation would be resulted the connectivity between active area and diode properties. So, our research would like to investigate the correlation between an active area study on the electrical, MS contact and photo-electrical characteristics of $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$ 10-MQW diode.

1.3 Research objective

The objectives of this research project are as follows:

(i) To simulate the effect of In and N fractions on the GaInNAs energy band gap transition using BAC modelling.

(ii) To analyse the optical and localisation defect characteristics of the $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$/GaAs 10-MQW thin film using temperature dependent PL spectroscopy.

(iii) To investigate the impact active area on the electrical, MS contact and photo-electrical properties of the $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$/GaAs 10-MQW p-i-n diode.

1.4 Research scope

The scopes of this research project are as follows:

(i) Analytical BAC modelling:

The analytical BAC modelling is used to estimate the energy band gap of GaInNAs with specific N and In fractions using Varshni's equation and Vegard law. The BAC modelling is developed using MATLAB as the simulation tool.

(ii) Sample growth and optical characterisation:

The samples were grown on an n-type GaAs (100) substrate using plasma-assisted molecular beam epitaxy (MBE). The intrinsic structure used in this work consists of 10 layers of 10-nm-thick $Ga_{0.925}In_{0.048}N_{0.016}As_{0.984}$ MQWs separated by a 10-nm GaAs barrier layer. The samples' growth was done at Tampere University of Technology, Finland, in collaboration with Optoelectronic and Terahertz Research Laboratory, University of Essex, UK. The percentage of the In and N fraction in GaInNAs composition has set to 4.8% and 1.6% to achieve an energy bandgap of 1.152 eV by referring to Vegard law. The sample that is characterised through the photoluminescence (PL) measurement is used to investigate the energy band gap of temperature-dependent GaInNAs (10–300 K) at specific wavelengths (700–1200 nm). The measurement was done at the

Institute of Microengineering and Nanoelectronics, National University of Malaysia. Moreover, the extended analysis of the PL peaks is used to determine the Varshni parameters and the localisation effect for GaInNAs materials.

(iii) Device fabrication and electrical and photo-electrical characterisations:
For device fabrication, a circular mesa structure of Ti-Au was coated on both tops as metal contacts by using the thermal evaporator with three dimensions of the optical window. There are six mesa active areas, ranging from 1.64 to 2.80 mm in diameter. The devices were fabricated at Optoelectronic and Terahertz Research Laboratory, University of Essex. The electrical and photo-electrical properties of the devices were evaluated through the current-voltage (I-V) measurement under dark and illumination conditions, respectively. The I-V measurement was conducted under dark and illumination conditions to obtain the dark I-V and illumination I-V characteristics, respectively. Moreover, the forward-bias dark I-V measurement was used to obtain the metal-semiconductor contact parameters through the thermionic emission (TE) theory. Whereas, the illumination I-V measurement was used to obtain the photovoltaic-mode parameters, such as short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and efficiency (η).

1.5 Summary of the chapter

The research backgrounds have been briefly explained the introduction about the development of a GaInNAs optoelectronic devices and the GaInNAs 10-MQW p-i-n diode for near-infrared range application. At that point, the story behind the Vegard law, BAC modelling, photocurrent oscillation and impact number of QWs had been elaborated to find the research gap in this study. So, that research gaps had stated in the problem statement to elucidate the contribution of the gap in GaInNAs optoelectronic. Then, all motivations have be declared in research objective to represent the mains direction on this study. Lastly, the general overview of methodology and boundaries in this research have elaborated in research scope subtopic.

CHAPTER 2

LITERATURE REVIEW

2.1 Dilute nitride material (GaInNAs)

In 1995, the first quaternary GaInNAs -based device was proposed to replace the InP-based device [16], [17]. A GaInNAs based device has the potential to overcome the drawbacks of the InP-based fabrication device in terms of the non-monolithic growth process and the refractive index of the InGaAsP/InP layer [3], [4]. The addition of In and N composition in GaAs induces the contraction of the lattice parameter, reduces the energy band gap and provides the lattice-matched GaInNAs/GaAs to operate in a certain wavelength range [13], as shown in Figure 2.1.

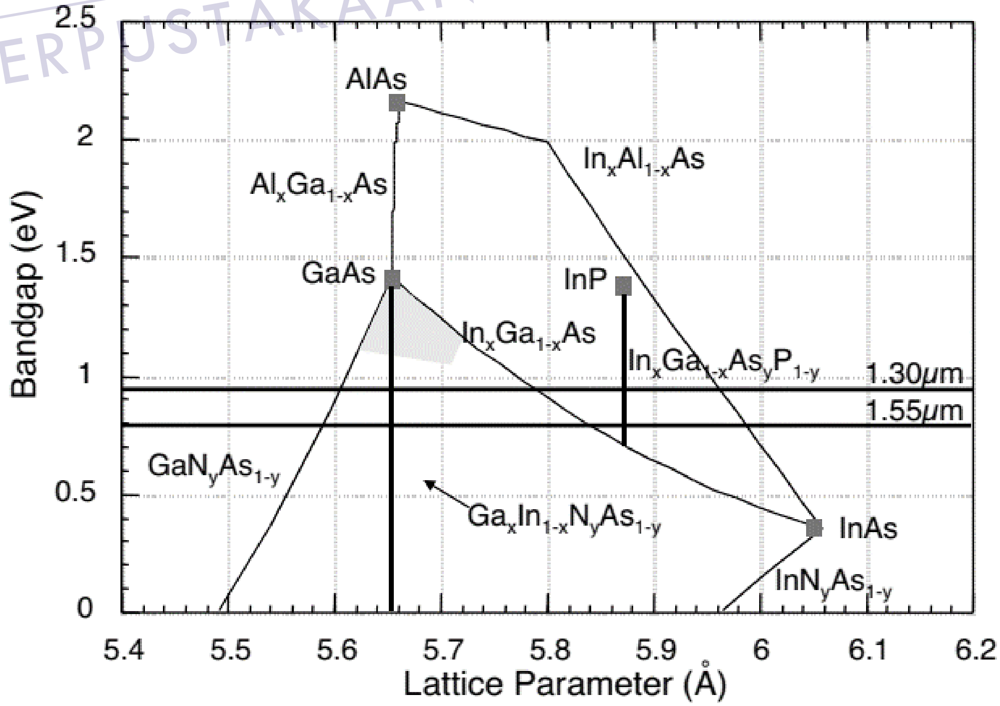

Figure 2.1: The band gap versus lattice constant for selected III-V alloys [18]

A huge number of academic research paper dedicated to reveal the potential of $Ga_{1-x}In_xN_yAs_{1-y}$ material system for optoelectronic applications are listed in Table 2.1.

Table 2.1: Comparative review of dilute-nitride optoelectronic devices

Type of study	Device design	Contribution	Application	References
Annealing effect on crystallinity properties	InGaAsN/GaAs $E_g = 1.0 - 1.4$ eV N-i-P junction	The annealing effect improves the crystallinity of dilute nitride material and also influences the dynamics of deep-level defects	Solar cell	[19]
The effect of top electrode of GaInNAs cell on electrical properties	p-i-n junction i-GaInNAs In: 16.2 N: 0.54 $E_g = 1.283$ eV	The correlation between the metal contact (top electrode) due to the photovoltaic performance	Solar cells	[20]
Modelling study of the quantum well's width and depth on photo-electrical converting efficiency	p-i-n junction i-GaInNAs In: 2.85% of N N: 0%–3%	The width of QWs is a key to improve photo-electric converting efficiency	Solar cell	[21]
Modelling the efficiency of GaNAsSb and GaInNAs single solar cells with different In and N compositions	p-i-n junction i-GaInNAs In: 0%–40% N : 1%–2.8% $E_g = 1.00$ eV	This modelling is also used to verify the compressive strain of thin film	Solar cells	[22]
Effect of V/III ratio during growth on the structural properties of 1.0-eV GaInNAs solar cells	p-i-n junction i-GaInNAs In: 7.8 % N: 2.8 % $E_g = 1.00$ eV	Reduction of V/III ratio during growth is able to influence the low effective doping concentration of p-type and n-type GaInNAs layers	Solar cell	[23]
Comparative studies of GaAs and GaInNAs MQW solar cells	n-i-p junction GaAs and GaInNAs/GaAs MQWs In: 3.0% N: 1.0% $E_g = 1.14$ eV	The MQWs increase the photo-response values and also increase dark current, leakage current and ideality factor	Solar cells	[24]
Effect of nitrogen composition on the GaInNAs photovoltaic properties as grown on GaAs substrate	GaInNAs/GaAs MQWs p-i-n junction In: 16% N fraction: 5.2%, 5.8%, 6.0%, 8.5% $E_g = 0.7 - 0.9$ eV	The higher N composition exhibits high crystalline of GaInNAs and good morphology structure. however, the dark current of devices risen due to the increase in the N composition	Solar cell	[25]

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